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(54) Electric cables comprising a semiconducting screening layer.

(57) In an electric cable for service at about 15kV and above, at least one extruded semiconductive screening layer comprises metal particles dispersed in a polymeric matrix. The matrix adheres both to the particles and to the insulation and at least the polymeric material in the matrix (normally in the insulation as well) is cross-linked by the technique involving grafting silane sidechains to the polymer and then cross-linking them by hydrolytic condensation (the "Sioplas-E" process). The proportion of dispersed conductive particles is sufficient to give a resistivity in a longitudinal direction of no more than 5000 ohm-cm. The resistivity of the metal of the particles does not exceed 15 times that of copper and its hardness is not greater than 100 Brinell. The particles have an average length of at least 1 mm (normally exceeding the thickness of the screening layer) and an aspect ratio of at least 10:1, and are predominantly aligned longitudinally of the cable. By selecting the particles in this way, conductivity is achieved with a material that is still extrudable, and the use of metal particles rather than conductive carbon black avoids the severe detrimental effects on the cross-linking process of moisture carried by the reactive surface of the carbon black.

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ELECTRIC CABLES

This invention relates to electric cables with polymeric insulation for service at moderately high voltages, say from about 10kV to about 150kV. At such voltages there is a risk of breakdown by local discharges occurring at the inner or outer surface of the insulation, and it is the practice to minimise this risk by applying to one or both those surfaces a thin layer of an electrically conductive material that will adhere more securely than would a metallic conductor. This layer generally has a resistivity much higher than that of a metal, and is consequently known as a "semiconductive" screen (though it has no connection with the "semiconductive" materials used in electronic devices).

In most modern designs of this kind of cable, the (or each) semiconductive screen is made of particles of a "conductive" grade of carbon black dispersed in a suitably chosen polymer. Serious problems sometimes arise, however, owing to the high adsorptive power of carbon black, which tends on the one hand to introduce moisture into the screen composition and on the other hand tends to withdraw additives from the polymer phase, which may be harmful owing to the presence of the additive at the carbon/polymer interface or to its loss from the polymer phase or both. These problems have been particularly acute when the polymeric material is to be cross-linked by the technique involving grafting silane side-chains to the polymer and then cross-linking them

by hydrolytic condensation, whether by the original two-stage process ("Sioplas-E") of Dow Corning Limited's British Patent No. 1286460 or the alternative improved single-stage processes of our British Patents Nos. 1526398 (jointly owned with Etablissements Maillefer S.A.) and 1534299. In this case moisture is extremely detrimental as it results in premature cross-linking and the silane reagents are very susceptible to adsorption, with consequent difficulties in controlling the eventual degree of cross-linking, and the gravity of the problem has been such that the use of this cross-linking technique in cables with semiconductive screens has been seriously inhibited.

The use of a metallic screen is not an acceptable alternative, because it cannot be kept in a sufficiently intimate contact with the insulation.

Semiconductive compositions can also be made by incorporating fine metallic particles in a polymeric matrix, and compositions of this kind have been proposed for certain screening purposes, as for example in US-A-3576387; but such compositions have such poor flow properties and are so highly abrasive that they cannot be extruded or applied by any other technique applicable to the screening of long lengths of cable.

More recently, for example in Polymer Engineering and Science, Volume 19 pages 1188 to 1192, polymeric-base screens containing relatively large metal particles of high aspect ratio have been described.

These screens however, were designed for electromagnetic screening of instruments and were made by injection moulding, with the particles randomly aligned; thus both the electrical and mechanical requirements were different from those appropriate to an extruded electrostatic screen in the cable industry.

We have now made the surprising discovery that sufficient of certain metallic particles can be introduced into silane-graft cross-linking compositions that remain extrudable by conventional techniques to establish conductance in the extruded screen.

The cable in accordance with the invention comprises at least one metallic conductor enclosed in insulation of a polymeric material of a sufficient radial thickness to withstand at least a D.C. potential of 15kV and, completely covering at least one of the inner and outer surfaces of the insulation, an extruded semiconducting screening layer comprising conductive particles dispersed in a matrix of a polymeric material which adheres both to the particles and to the insulation, the polymeric material in the matrix at least being cross-linked by the technique involving grafting silane side-chains to the polymer and then cross-linking them by hydrolytic condensation and the proportion of dispersed conductive particles being sufficient to give a resistivity (measured in the direction of the length of the cable) of no more than 5000 ohm-cm, and is distinguished by the fact that the conductive particles

are of a metal with a resistivity not exceeding 15 times that of annealed copper and a hardness not greater than 100 Brinell and have an average length of at least 1 mm and an aspect ratio of at least 10:1 and a predominant alignment longitudinally of the cable.

By the aspect ratio of a particle is meant the ratio of its length to its shortest dimension perpendicular to its length, for example in the case of a cylindrical fibre (a preferred shape) the ratio of length to diameter and in the case of a flake the ratio of length to thickness. Both fibres and flakes are commercially available (for instance from Transmet Corporation of Columbus, Ohio, USA); they are mostly made by the "melt-extraction" and "melt drag" techniques developed by Battelle Laboratories Inc., (also of Columbus, Ohio), but fibres can also be made by chopping fine wire.

There is no clearly defined upper limit to the length of the particles but our present preference is for particles with a length up to about 20 mm and more especially up to about 6 mm. It will be noted that the lengths of the particles are many times greater than those of conductive carbon particles (typically of the order of micrometres) and will almost always exceed the thickness of the screening layer. The extrusion process aligns the particles to such an extent that there is no significant risk that they will extend through the whole thickness of the layer.

Preferably the particles are of aluminium or a dilute aluminium alloy having resistivities relative to

copper in the range 1.6 to 2.0 times and hardness in the range 15 to 40 Brinell. Other metals that may be used include lead (12.5 and 5), zinc (3.5 and 50), copper (1 and 50) and subject to cost considerations tin (6.6 and 10), nickel (4.1 and 100) and silver (0.95 and 60). Composite particles, such as tinned or nickel-plated copper and silvered aluminium can be used, as may mixtures of particles of different metals (and/or composites).

The proportion of particles to matrix required will vary with the material shapes and sizes of the particles, with the degree of orientation brought about by extrusion (which can be increased by using a long-land extrusion die, preferably with a passage that reduces in cross-section towards the outlet) and to some extent with the nature of the matrix polymer. In most cases less than 10% by volume will be needed.

Conventional cable-making polymers (and compatible mixtures) that are suitable for cross-linking with silanes can be used for the matrix; when the cable insulation is of polyethylene (which will in most cases be cross-linked by the same silane-grafting technique), we prefer to select the matrix polymer from:

(1) alkene homopolymers such as polyethylene and polypropylene;

(2) alkene copolymers such as ethylene-propylene rubbers (including terpolymers of the "EPDM" type); and

(3) polar copolymers of ethylene with unsaturated esters, e.g. vinyl acetate, ethyl acrylate, or butyl acrylate.

The polar copolymers are especially preferred as they adhere strongly to the metal surfaces and adhere to the insulation sufficiently, but not so strongly as to make stripping difficult.

It is thought that the compatibility of the metal particles with the matrix is improved by the presence of the silane reagents, but if desired they may be treated with a specific adhesion promotor, such as a functional organosilane or organotitanate.

The matrix polymer may of course be compounded with other appropriate ingredients, such as cross-linking additives, stabilisers, antioxidants and copper inhibitors; carbon black (conductive or reinforcing) may be used in small amounts and may in some cases be used to increase radial conductivity of the screening layer; large quantities of carbon black are, of course, undesirable.

Examples

A series of 33kV power cables is made using the general procedure and the insulation composition of Example 1 of Specification No. 1526398. Both surfaces of the insulation are coated with a thin semiconductive screening layer

Example 1

The screening layers are of the following formulation (in parts by weight):

Polyethylene, density 0.92, melt-flow index 2	100
Aluminium alloy fibres, made by melt extraction, with an average length of 3 mm and aspect ratio 35, resistivity 1.6 times that of annealed copper, hardness 25 Brinell.	20
Dicumyl peroxide) (grafting agents)	0.1
Vinyl trimethoxysilane)	1.5
Polymerised trimethyl dihydroquinoline (Flectol H) (antioxidant)	0.5
Dibutytin dilaurate (condensation catalyst)	0.05

These ingredients are metered directly into the screening extruder, blended and grafted therein and extruded through tapering long-land dies by a pull-down technique, the diameter of each die orifice being about 1.5 times the final diameter of the screening layer. The thickness of each of the screening layers was about 1 mm.

This formulation has a volume resistivity of about 100 ohm-cm, and in the hot set test specified in IEC 502 at 200°C has an elongation of about 100%.

Example 2

This is similar to Example 1 except that the aluminium alloy fibres are pre-dispersed in 10 parts of the polyethylene using a Banbury mixer. This produces a more uniform dispersion but some fibres are deformed in the mixing process and the average conductivity is a little lower.

Example 3

100 aluminium wires, nominally 0.025 mm in diamater (produced by the technique of our UK Patent No. 1394058) are formed into a bunch and thinly sheathed with polyethylene. The sheathed bunch is then chopped into 8 mm lengths to give fibres with an aspect ratio of about 320 in compact granules with minimal trapped air that readily mix with granulated polyethylene. They are tumble-mixed with such polyethylene granules in proportions to give 15 parts by weight of aluminium to 100 parts total polyethylene; the same grafting agents, antioxidant and catalyst are metered in at the extruder as before, and the subsequent procedure is the same.

Example 4

180 copper wires with a nominal diameter of 0.0075 mm are bunched and the bunch chopped, without sheathing, into random lengths between 3 and 18 mm giving aspect ratios in the approximate range 400 to 2400. These fibres are tumble-mixed until reasonably uniformly dispersed. 10 parts by weight of this mixture are substituted for the 20 parts of aluminium fibres in the formulation of Example 1.

The techniques of Examples 3 and 4 provide an outlet for very fine drawn wires that are unsuitable for their intended purpose (e.g. because, through breakages, they do not meet the customer's specification for supply length).

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Exampl 5

A formulation comprising, in parts by weight:

Ethylene-vinyl acetate copolymer (28% vinyl acetate by weight, melt flow index 5)	100
Aluminium alloy fibres (average length 6mm, average aspect ratio 90)	15
Dicumyl peroxide	0.1
Vinyl trimethoxy silane	1.2
Flectol H	0.5
Dibutyl tin dilaurate	0.05

was used in place of the formulation set out in Example 1 to make a readily strippable screen.

CLAIMS

1. An electric cable comprising at least one metallic conductor enclosed in insulation of a polymeric material of sufficient radial thickness to withstand at least a D.C. potential of 15kV and, completely covering at least one of the inner and outer surfaces of the insulation, an extruded semiconducting screening layer comprising conductive particles dispersed in a matrix of a polymeric material which adheres both to the particles and to the insulation, the polymeric material in the matrix at least being cross-linked by the technique involving grafting silane side-chains to the polymer and then cross-linking them by hydrolytic condensation and the proportion of dispersed conductive particles being sufficient to give a resistivity (measured in the direction of the length of the cable) of no more than 5000 ohm-cm, distinguished by the fact that the conductive particles are of a metal with a resistivity not exceeding 15 times that of annealed copper and a hardness not greater than 100 Brinell and have an average length of at least 1 mm and an aspect ratio of at least 10:1 and a predominant alignment longitudinally of the cable.

2. A cable as claimed in Claim 1 in which the particles are fibres.

3. A cable as claimed in Claim 1 or Claim 2 in which the particles have a length in the range 1-20 mm.

4. A cable as claimed in Claim 1 or Claim 2 in which the particles have a length in the range 1-6 mm.

5. A cable as claimed in any one of the preceding claims characterised in that the particles are of aluminium or an aluminium alloy.

6. A cable as claimed in any one of the preceding claims in which the particles are made by a "melt extraction" or "melt drag" technique.

7. A cable as claimed in any one of Claims 1 to 5 in which the particles are of chopped fine wire.

8. A cable as claimed in any one of the preceding claims in which the metal particles have been treated with an adhesion promotor such as a function organosilane or organotitanate.

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EUROPEAN SEARCH REPORT

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Application number

EP 81 30 4385

Category	DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
	CH - A - 477 072 (MINNESOTA MINING AND MANUFACTURING) * Column 2, line 13 - column 10, line 58; figures 1-6 * --	1,5	H 01 B 9/02 1/22
	FR - A - 2 286 160 (EATON) * Page 7, line 19 - page 11, line 1; figures 1-8 * --	1,2,5	
	FR - A - 1 479 767 (GAISER et al.) * Page 1, column 2, paragraph 2 - page 3, column 2, paragraph 7; figures * --	1,5	TECHNICAL FIELDS SEARCHED (Int. Cl.³) H 01 B 9/02 11/10 1/22 3/00 5/16
	BE - A - 882 633 (DART INDUSTR.) * Page 4, paragraph 4 - page 13, claim 8 * --	1-5	
	DE - A - 2 740 195 (TORAY) * Claims 1-7; figure 1 * --	1,2,5	
EP	GB - A - 2 056 994 (LEVY) * Claims 1-7 * --	1,3-5	CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
A	US - A - 3 666 876 (ESSO) * Column 2, line 21 - column 8, line 42; figures 1-3 * -- ./.	1,5	
X	The present search report has been drawn up for all claims		&: member of the same patent family, corresponding document

Place of search	Date of completion of the search	Examiner
The Hague	24-12-1981	DEMOLDER

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
AD	US - A - 3 576 387 (DERBY) * Column 2, line 46 - column 10, line 57;, figure 3 * ----	1,5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.³)